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(71) Applicant: **Exxon Research and Engineering Company, P.O.Box 390 180 Park Avenue, Florham Park New Jersey 07932 (US)**

(72) Inventor: **Feldman, Nicholas, 48 Hunter Lane, Woodbridge New Jersey 07095 (US)**

(74) Representative: **Pitkin, Robert Wilfred et al, ESSO Engineering (Europe) Ltd. Patents & Licences Apex Tower High Street, New Malden Surrey KT3 4DJ (GB)**

(54) **Middle distillate fuel flow improver composition.**

(57) An additive composition for improving the low temperature flow properties of a wax-containing petroleum distillate fuel comprises:

A. an amide and/or amine salt of a carboxylic acid and/or anhydride;

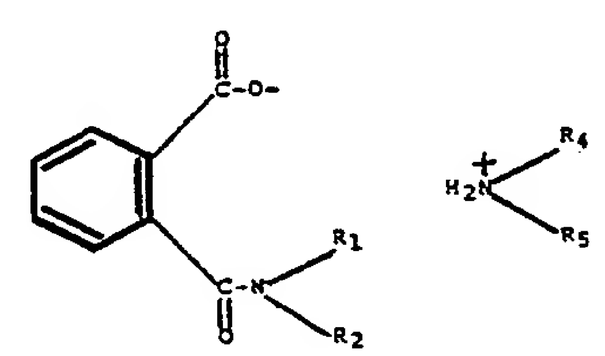
B. an ethylene polymer and/or copolymer;

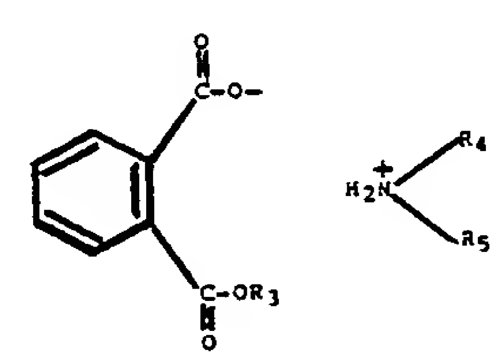
C. a condensation product of a halogenated paraffin or an olefin with an aromatic compound;

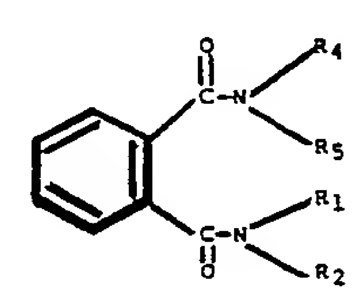
D. an alkylated diphenyl ether.

Examples of each component are (A) tetraalkyl ammonium phthalamate, (B) ethylene vinyl acetate, (C) a wax-naphthalene condensate, and (D) diphenyl ether alkylated with a dimer of a C_{24} alpha olefin.

Preferred treat rates are from 0.01 to 0.15 wt % of (A); 0.005 to 0.5 wt % of each of (B) and (D); and 0.002 to 0.1 wt % of (C), each based on the fuel, which is preferably one having a boiling range within the limits 120°C and 450°C.







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Background of the Invention

This invention is related to wax-containing petroleum distillate having improved low temperature flow properties. More specifically, the present invention is related to a wax-containing middle distillate fuel oil having a boiling range within the limits of about 120°C and about 450°C.

The problem of improving the cold flow properties of wax-containing distillates has become more pronounced recently because of increases in the demand for certain petroleum products, including kerosene and the middle distillates. Kerosene, which acts as a solvent for n-paraffin wax, normally had been a component of middle distillate fuel oils. The increased demand for kerosene in jet fuels has reduced the amount of kerosene available for use in middle distillate fuel oils. In addition, the increased demand for middle distillate fuel oils, particularly diesel fuel, while demand for gasoline has remained essentially flat, has made it attractive to maximize the production of middle distillates.

The wax present in middle distillates precipitates at low temperature, forming large waxy crystals which tend to plug the small pore openings of fuel filters. This problem is particularly acute for diesel fuels, where the openings in the fuel filter typically are between about 5.0 and about 50 microns. Conventional pour depressants, which lower the pour point, i.e. the point at which the fuel can no longer be poured, may not be completely satisfactory for pre-

venting pluggage of the fuel filters. While pour depressants often prevent the fuel from setting up as a gel, large wax crystals may be formed. However, to improve the cold flow properties of wax-containing middle distillate fuels oils so that the wax does not plug the fuel filter pores, it is necessary that only fine wax crystals be formed.

Considerable work has been directed at additives which improve the cold flow properties of the wax-containing middle distillate fuels. U.S. Patent No. 3,790,359 is directed at the addition of from about 0.1 to about 3 weight percent of an essentially saturated hydrocarbon fraction substantially free of normal paraffinic hydrocarbons having a number average molecular weight in the range of about 600 to about 3,000, in combination with a copolymer of ethylene and an unsaturated ester, where the copolymer has less than 6 methyl terminating side branches per 100 methylene groups. The weight ratio of the saturated hydrocarbon-fraction to the copolymer was disclosed to range between about 25:1 to about 1:1.

U.S. Patent No. 3,999,960 discloses the use of ethers, particularly alkyldiphenylether, to improve the cold flow properties of wax-containing middle distillate fuels.

U.S. Patent No. 3,883,318 describes the combination of wax-naphthalene and ethylene vinyl acetate as a pour depressant for middle distillate fuels.

U.S. Patent No. 3,982,909 discloses the combination of (a) maleic acid monoamides of hydrogenated tallow amine neutralized with the same amine; (b) an ethylene-vinyl acetate copolymer; and (c) a wax-naphthalene condensate produced a cold flow improver for middle distillate fuels.

U.S. Patent No. 4,014,663 discloses the combination of (a) an alkylated diphenyl ether with (b) the reaction product of hydrogenated tallow amine and alkenylsuccinic anhydride.

U.S. Patent No. 3,910,776 discloses the combination of (a) ethylene and an unsaturated ester; and (b) the condensation product of wax and naphthalene in improving the cold flow properties of distillate petroleum fuels.

U.S. Patent No. 4,402,708 discloses the use of oil-soluble dialkyl amine derivatives, such as salts of phthalic anhydride as low temperature flow improvers for middle distillate fuels.

With the increasing demand for middle distillate fuels it is advantageous to maximize the production of middle distillates. Therefore, the middle distillate fuels are expected to have n-paraffinic wax contents at least as great as are presently found. Frequently, these fuels having high wax appearance points do not respond well even to combinations of additives, such as those noted above.

Other additives have been utilized which contain amorphous wax from petroleum derived products, such as Foots oil or petrolatum in combination with a synthetically prepared wax crystal modifier. However, amorphous wax has to be used at relatively high treat rates of about 0.2 to about 0.3 weight percent, is difficult to dissolve in the middle distillate fuel and is not always available. In addition, the composition of the wax may vary widely, which may affect its utility.

Accordingly, it is desirable to provide an additive comprising synthetically prepared components for improving the low temperature flow properties of middle distillate fuels.

It also is desirable to provide a middle distillate fuel additive for improving the low temperature flow properties which is relatively inexpensive and which is effective at relatively low treat rates.

It also is desirable to provide an additive which did not significantly affect the combustion properties of the fuel.

The present invention is directed at the addition to a middle distillate fuel of an additive comprising:

A. an amide and/or amine salt of carboxylic acid and/or anhydride;

B. an ethylene-containing polymer and/or copolymer;

C. a wax-naphthalene condensation product; and

D. an alkylated diphenyl ether.

Summary of the Invention

The present invention is directed at a wax-containing petroleum distillate fuel having a boiling range between about 120°C and about 450°C which has improved low temperature flow properties by the addition thereto of:

A. an amide and/or amine salt of carboxylic acid and/or anhydride;

B. an ethylene-containing polymer and/or copolymer;

C. a wax-naphthalene condensation product; and

D. an alkylated diphenyl ether.

The amide and/or amine salt of carboxylic acid and/or anhydride preferably is selected from the group consisting of oil soluble amine salts and/or amides which generally will be formed by reaction of at least one molar proportion of hydrocarbyl substituted amines with a molar proportion of hydrocarbyl acid having 1-4 carboxylic acid groups or their anhydrides. The ethylene-containing polymer preferably is selected from the group of polymers consisting of ethylene vinyl acetate and ethylene vinyl chloride. The wax-naphthalene condensation product preferably is selected from the group of condensation products consisting of

chlorinated n-paraffin waxes condensed with naphthalenes. The diphenyl ether preferably is alkylated with a compound selected from the group consisting of dimers of alpha olefins having from about 16 to about 40 carbon atoms.

The present invention also is directed at a method for improving the low temperature flow properties of a middle distillate fuel boiling in the range of about 120°C to about 450°C, which comprises adding to the middle distillate fuel an effective amount of an additive comprising:

A. an amide and/or amine salt of carboxylic acid and/or anhydride;

B. an ethylene-containing polymer and/or copolymer;

C. a wax-naphthalene condensation product; and

D. an alkylated diphenyl ether.

In a preferred embodiment the additive comprises at least about 0.005 weight percent of the fuel to about 2.0 weight percent of the fuel, and preferably ranges between about 0.03 weight percent and 0.50 weight percent of the middle distillate fuel.

The additive may be added to the middle distillate fuel as a concentrate in which a heavy aromatic naphtha preferably is present as a diluent. The preferred concentration ranges of the various components in the concentrate are as follows:

COMPONENT	WEIGHT PERCENT RANGE	PREFERRED WEIGHT PERCENT RANGE
A. Amide and/or Amine Salt of Carboxylic Acid/Anhydride	5-40	12-25
B. Ethylene-containing Polymer/Copolymer	2-15	3-10
C. Wax-Naphthalene Condensation Product	1-10	1-3
D. Alkylated Diphenyl Ether	2-15	4-12
E. Diluent	20-95	35-75

The multi-component additive may be added to the distillate fuel at any point which will assume good mixing of the additive with the middle distillate fuel.

Detailed Description of the Invention

As used herein the term "middle distillate fuels" refers to fuels having an atmospheric boiling point ranging between about 120°C and about 450°C, preferably ranging between about 120°C and about 425°C, more preferably between about 120°C, and about 400°C, and most preferably between about 135°C and about 360°C. Commonly used middle distillate fuels comprise diesel fuel, Number 2 fuel oil, kerosene and turbine fuel.

The present invention is directed at the combination of an additive comprising:

A. an amide and/or amine salt of carboxylic acid/anhydride;

B. a wax modifying random polymer/copolymer of ethylene;

C. a wax-naphthalene condensation product; and

D. an alkylated diphenyl ether.

for improving the cold flow properties of a wax-containing middle distillate fuel.

The preparation and composition of each of these compounds is set forth below:

A. Amide and/or Amine Salt of Carboxylic Acid/Anhydride

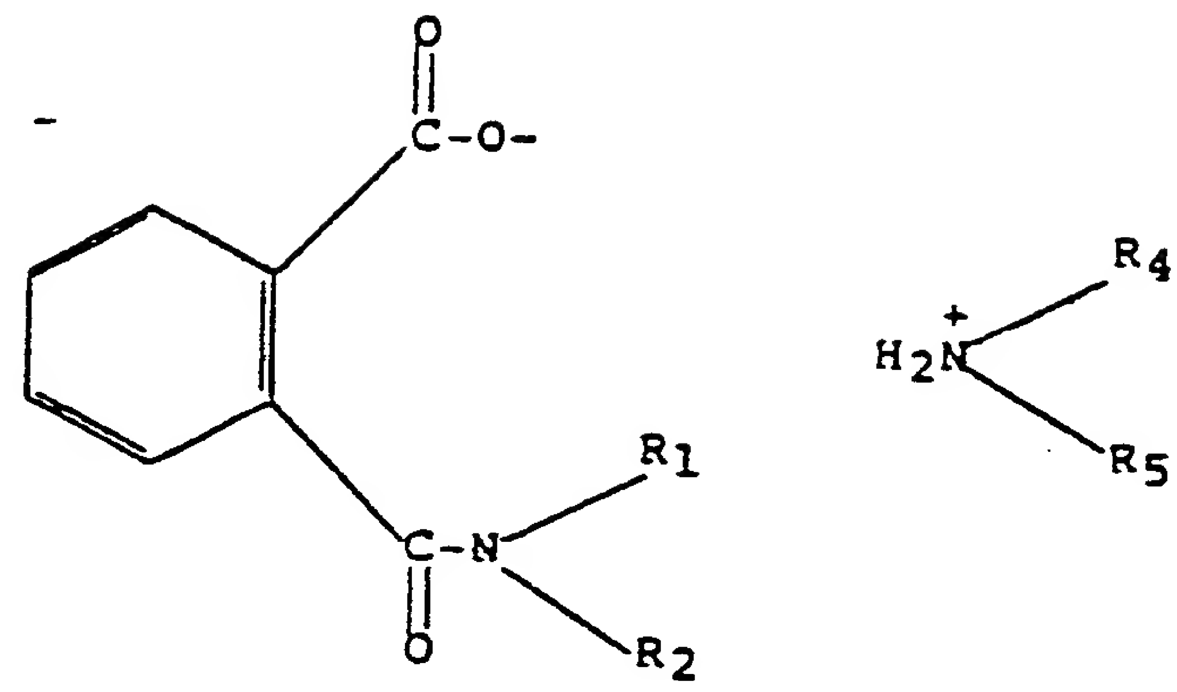
The preparation of the amides and/or amine salts of carboxylic acid/anhydride is described in U.S. Patent No. 4,402,708, the disclosure of which is incorporated herein by reference. The alkyl amine salts of phthalic anhydride and maleic anhydride are particularly preferred, with an alkyl amine salt of phthalic anhydride being especially preferred. The alkyl amine salt of phthalic anhydride can be readily formed by the reaction of phthalic anhydride or its monoester, with alkyl amines, preferably secondary

alkyl amines so as to form compounds having a minimum of three $C_{16}-C_{40}$, preferably $C_{16}-C_{24}$ alkyl or alkenyl groups, more preferably alkyl groups, of which at least two of said alkyl groups are of said secondary amine. Preferably at least one, and more preferably all, of the alkyl groups are straight chain.

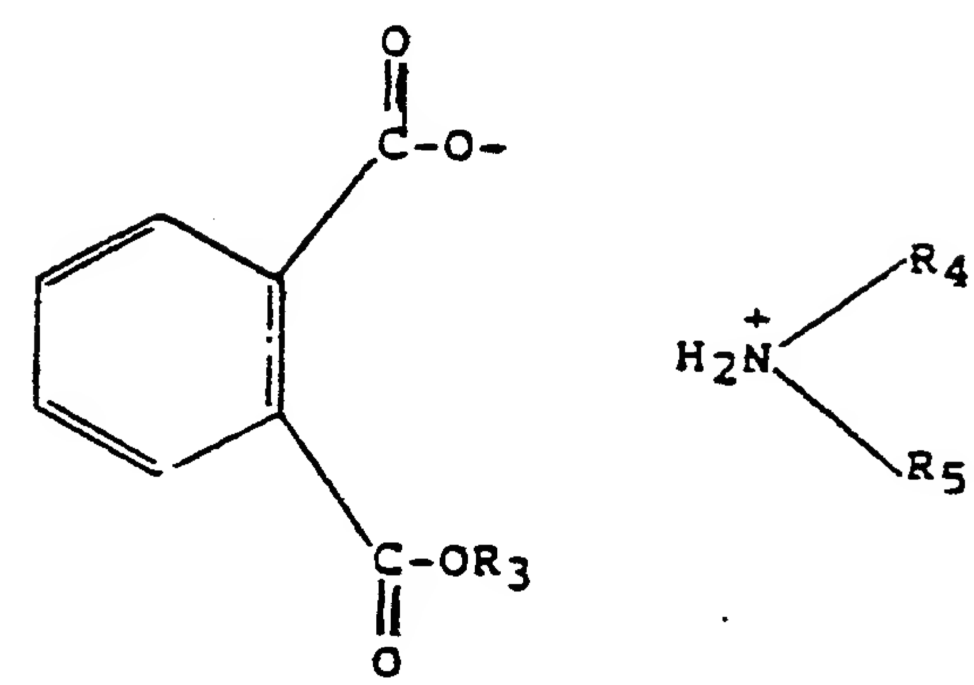
Examples of $C_{16}-C_{40}$, preferably $C_{16}-C_{24}$ alcohols that can be used to make the monoester include 1-hexadecanol, 1-octadecanol, stearyl alcohol, behenyl alcohol, ceryl alcohol, tricosanol, etc.

Examples of $C_{16}-C_{40}$ secondary amines include N,N-dihexadecyl amine; N,N-dioctadecyl amine; N-hexadecyl; N-octadecyl amine; N,N-dieicosenyl amine; N,N-distearyl amine; N,N-dibehenyl amine; etc. A particularly useful amine is di-hydrogenated tallow amine, wherein the N-alkyl groups are derived from tallow fat, of which a typical composition is about 3% $C_{14}H_{29}$, about 34 weight percent $C_{16}H_{33}$ and about 63 weight percent $C_{18}H_{37}$ alkyl groups.

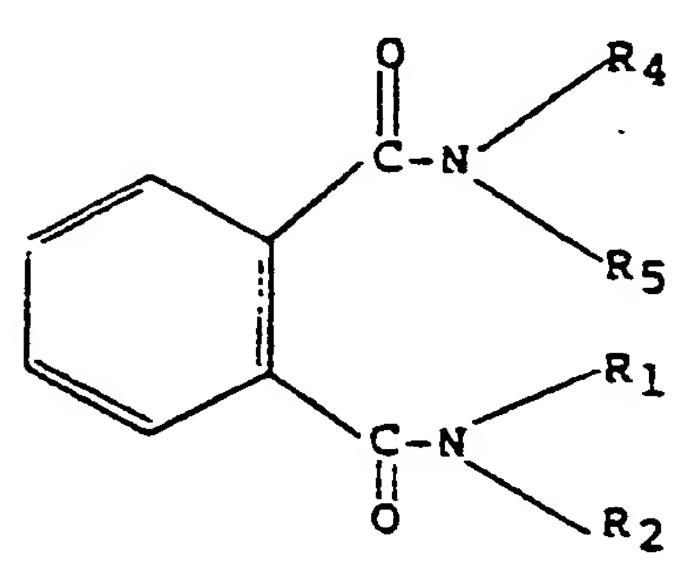
Particularly preferred are the following orthophthalic derivatives:



tetraalkyl ammonium phthalamate particularly preferred,



dialkyl ammonium monoalkyl phthalate, and



tetraalkyl phthalamide,

wherein R_1, R_2, R_4 and R_5 are the C_{16}-C_{40}, preferably C_{16}-C_{24} straight chain alkyl groups of the secondary amine, and may be the same or different, and R_3 is the C_{16}-C_{40}, preferably C_{16}-C_{24} straight chain alkyl group of the alcohol. In it most preferred form, R_1, R_2, R_4 and R_5 are alkyl groups derived from tallow amine as discussed above.

The amides can be formed in a conventional manner by heating the secondary amine with the ortho phthalic acid or acid anhydride. Similarly, the ester is prepared in a conventional manner by heating the alcohol and the acid or the anhydride to partially esterify the acid or anhydride (so that one carboxyl group remains for the reaction with the amine to form the amide or amine salt). The ammonium salts are also conventionally prepared by simply mixing the amine with the acid or acid anhydride, or the partial ester of a polycarboxylic acid, or partial amide of a polycarboxylic acid, with stirring, generally with mild heating.

B. Wax Modifying Ethylene Containing Polymer/Copolymer

Wax modifying ethylene-containing polymers/copolymers are described in U.S. Patent No. 3,910,776, the disclosure of which is incorporated herein by reference.

In general, these polymeric pour depressants have a polyethylene backbone which is divided into segments by hydrocarbon or oxy-hydrocarbon side chains. These oil-soluble polymers will generally have a number average molecular weight in the range of about 500 to 50,000, preferably about 1,000 to about 5,000, as

measured for example, by Vapor Pressure Osmometer, such as using a Mechrolab Vapor Pressure Osmometer Model 310A. Generally, they will comprise about 3 to 40, preferably 4 to 20, molar proportions of ethylene per molar proportion of a second ethylenically unsaturated monomer, which latter monomer can be a single monomer or a mixture of such monomers in any proportion.

The unsaturated monomers, copolymerizable with ethylene, include unsaturated mono and diesters of the general formula:

$$\begin{array}{ccc} R_1 & & H \\ | & & | \\ C & = & C \\ | & & | \\ R_2 & & R_3 \end{array}$$

wherein R_1 is hydrogen or methyl; R_2 is a $-OOCR_4$ or $-COOR_4$ group wherein R_4 is hydrogen or a C_1 to C_{16}, preferably C_1 to C_4, straight or branched chain alkyl group; and R_3 is hydrogen or $-COOR_4$. The monomer, when R_1 and R_3 are hydrogen and R_2 is $-OOCR_4$ includes vinyl alcohol esters of C_2 to C_{17} monocarboxylic acids, preferably C_2 to C_5 monocarboxylic acid. Examples of such esters include vinyl acetate, vinyl isobutyrate, vinyl laurate, vinyl myristate, vinyl palmitate, etc. When R_2 is $-COOR_4$, such esters include methyl acrylate, isobutyl acrylate, methyl methacrylate, lauryl acrylate, C_{13} Oxo alcohol esters of methacrylic acid, etc. Examples of monomers where R_1 is hydrogen and R_2 and R_3 are $-COOR_4$ groups, include mono and diesters of unsaturated dicarboxylic acids such as: mono C_{13} Oxo fumarate, di-C_{13} Oxo fumarate, di-isopropyl maleate; di-lauryl fumarate; ethylmethyl fumarate; etc.

Another class of monomers that can be copolymerized with ethylene include C_3 to C_{16} alpha monoolefins, which can be either branched or unbranched, such as propylene, isobutene, n-octene-1, isooctene-1, n-decene-1, dodecene-1, etc.

Particularly preferred ethylene-containing polymers comprise ethylene vinyl acetate and ethylene vinyl chloride.

Still other monomers include vinyl chloride, although essentially the same result can be obtained by polyethylene chlorinated to contain about 5 to 35 weight percent chlorine.

These polyethylene and ethylene copolymer pour depressant components are generally formed using a free radical promoter, or in some cases they can be formed by thermal polymerization, or they can be formed by Ziegler type polymerization in the case of ethylene with other olefins. The polymers produced by free radical polymerization appear to be the more important and can be formed as follows: Solvent, and 0-50 weight percent, of the total amount of monomer other than ethylene, e.g. an ester monomer, used in the batch, are charged to a stainless steel pressure vessel which is equipped with a stirrer and cooling coil. The temperature of the pressure vessel is then brought to the desired reaction temperature, e.g. 70° to 250°C, and pressured to the desired pressure with ethylene, e.g. 800 to to 10,000 psig, usually 900 to 6,000 psig. Then promoter, usually diluted with the reaction solvent, and additional amounts of the second monomer, e.g. unsaturated ester, are added to the vessel continuously, or at least intermittently, during the reaction

time, which continuous addition gives a more homogeneous copolymer product as compared to adding all the unsaturated ester at the beginning of the reaction. Also during this reaction time, as ethylene is consumed in the polymerization reaction, additional ethylene is supplied through a pressure controlling regulator so as to maintain the desired reaction pressure fairly constant at all times. Following the completion of the reaction, usually a total reaction time of 1/4 to 10 hours will suffice, the liquid products are withdrawn from the pressure vessel, and the solvent removed by stripping, leaving the polymer as residue.

C. Wax-Naphthalene Condensation Product

The wax-naphthalene condensation product is described in U.S. Patent No. 3,910,776, the disclosure of which is incorporated herein by reference.

These materials are usually made by the Friedel-Crafts condensation of a halogenated paraffin or an olefin with an aromatic hydrocarbon. They are well known in the art, primarily as lube oil pour depressants and as dewaxing aids. Usually, the halogenated paraffin will contain from about 15 to 60, e.g. 16 to about 50 carbons, and from about 5 to about 25 weight percent, e.g. 10 to 18 weight percent, chlorine. Typically, the halogenated paraffins are prepared by chlorinating to the above recited chlorine content a paraffin wax having a melting point within the range of about 100° to 200°F. The aromatic hydrocarbon used usually contains a maximum of three substituent groups and/or condensed rings. It may be a hydroxyl compound such as phenol, cresol, xylenol, or an amine such as aniline, but is preferably naphthalene, phenanthrene or anthracene.

Particularly preferred wax-naphthalene condensation products comprise the condensation product of chlorinated n-paraffin wax and naphthalene.

D. Alkylated Diphenyl Ether

The alkylated diphenyl ethers may be prepared by alkylating diphenyl ether with dimerized or polymerized -olefins as described in U.S. Patent No. 3,999,960, the disclosure of which is incorporated herein by reference. Preferred ether compounds are diphenyl ethers alkylated with an alpha olefin having from about 16 to about 50 carbon atoms or with a dimer of an alpha olefin that has from about 16 to about 40 carbon atoms.

The following examples demonstrate the utility of the present invention in improving the cold flow properties of a middle distillate fuel.

The additives listed in Table I were added to a wax containing middle distillate fuel having a Wax Appearance Point (WAP) of -13.3°C (+8°F) maintained at about 25°C. This fuel was designated as Fuel A. A test has been devised which has been found to be a relatively accurate indicator of cold flow performance of fuels in passing through fuel filters. In this test, designated as Low Temperature Filterability Test (LTFT) the test fuel is cooled at a rate of 1°C/hour to the desired test temperature and subsequently is passed through a screen having openings 17 microns in diameter under a pressure of 6 inches of mercury. The fuel is determined to pass the test if the fuel flow through the screen is completed in 60 seconds or less.

In these tests the amide and/or amine salt of carboxylic acid/anhydride comprised a dihydrogenated tallow amine salt of phthalic anhydride in which two moles of the amine are reacted with one mole of phthalic anhydride.

The ethylene-containing polymer/copolymer comprised a mixture of two ethylene-vinyl acetate copolymers, having different oil solubilities, so that one functions primarily as a wax growth arrestor and the other as a nucleator, in accord with the teachings of U.S. Pat. No. 3,961,916 which patent is hereby incorporated herein in its entirety. More specifically, the ethylene-containg polymer/copolymer is a polymer mixture of about 75 wt. % of wax growth arrestor and about 25 wt. % of nucleator.

The wax growth arrestor was a copolymer of ethylene and about 38 wt. % vinyl acetate, and had a number average molecular weight of about 1800 as determined by Vapor Phase Osometry (VPO). It is identified in said U.S. Pat. No. 3,961,916 as Copolymer B of Example 1 (column 8, lines 25-35).

The nucleator was a copolymer of ethylene and about 16 wt. % vinyl acetate and had a molecular weight of about 3000 (VPO). It is identified in said U.S. Pat. No. 3,961,916 as Copolymer H (see Table I, columns 7-8).

The wax naphthalene condensation product comprised the condensation product of 100 parts by weight n-paraffin wax having a melting point of about 163°F chlorinated to about 12 weight percent chlorine condensed with about 8.8 weight parts by weight naphthalene.

The alkylated diphenyl ether comprised a diphenyl ether alkylated with a dimer of an alpha olefin having about 24 carbon atoms. The fuel utilized in all of the following Comparative Examples and Examples had a boiling range of about 120°C to about 400°C.

Comparative Example 1

In the first series of comparative tests Fuel A was utilized without any additives. The lowest temperature at which this fuel passed the LTFT test was -14°C.

Comparative Example 2

In this test 0.06 weight percent of the previously described ethylene vinyl acetate copolymer (EVA) and 0.015 weight percent wax naphthalene condensate (WNC) and 0.025 weight percent alkyl-diphenyl ether (ADPE) were added to the fuel. The lowest temperature at which this sample passed the LTFT test was -17°C.

Comparative Example 3

In this test, 0.035 weight percent of a dihydrogenated tallow amine salt of phthalic anhydride (TAPA) 0.015 weight percent ethylene vinyl acetate copolymer and 0.02 weight percent of alkyl-diphenyl ether were added to Fuel A. The lowest temperature at which this sample passed the LTFT test was -19°C.

Comparative Example 4

In this test 0.035 weight percent of dihydrogenated tallow amine salt of phthalic anhydride

0.02 weight percent ethylene vinyl acetate, and 0.005 weight percent wax-naphthalene condensate were added to Fuel A. The lowest temperature at which this sample passed the LTFT test was -18°C.

Comparative Example 5

In this test 0.05 weight percent dihydrogenated tallow amine salt of phthalic anhydride and 0.025 weight percent alkylated diphenyl ether were added to Fuel A. The lowest temperature at which this fuel sample passed the LTFT test was -19°C.

Example I

In this example 0.025 weight percent dihydrogenated tallow amine of phthalic anhydride, about 0.008 weight percent ethylene vinyl acetate, 0.002 weight percent wax-naphthalene condensation product, and 0.01 weight percent alkyl-diphenyl ether were added to Fuel A. This combination passed LTFT tests at temperatures as low as -22°C thereby demonstrating the utility of the present invention.

A summary of the LTFT test results on Fuel A in Comparative Examples 1-5 and in Example I is presented in Table I. This table demonstrates that the use of the four component system produced a fuel oil having a lower LTFT than any of the comparative examples even though the total weight percent of additive used with the four component system was lower than the weight percent of additive used in Comparative Examples 2-5.

TABLE I

TEST DESC.	WEIGHT PERCENT ADDITIVE IN FUEL				TOTAL WT. % ADDITIVE IN FUEL	LOWEST TEMPERATURE FOR LTFT PASS, °C
	TAPA	EVA	WAX-NAPHTHALENE	ADPE		
Comp. E.G. 1	-	-	-	-	-	-14°C
Comp. E.G. 2		0.06	0.015	0.025	0.100	-17°C
Comp. E.G. 3	0.035	0.015		0.02	0.070	-19°C
Comp. E.G. 4	0.035	0.02	0.005		0.060	-18°C
Comp. E.G. 5	0.05			0.025	0.075	-19°C
Example I	0.025	0.008	0.002	0.01	0.045	-22°C

A series of tests also were conducted on a second fuel sample, Fuel B, having a Wax Appearance Point of -7.8°C (+18°F).

Comparative Example 6

When no additives were added to Fuel B, the lowest temperature at which the fuel passed the LTFT test was -9°C.

Comparative Example 7

In this test 0.05 weight percent of dihydrogenated tallow amine salt of phthalic anhydride, 0.02 weight percent of ethylene vinyl acetate copolymer, and 0.005 weight percent of wax-naphthalene condensation product were added to Fuel B. The lowest temperature at which the fuel passed the LTFT test was -13°C.

Comparative Example 8

In this test about 0.038 weight percent of ethylene vinyl acetate copolymer, about 0.012 weight percent wax naphthalene condensation product and 0.025 weight percent alkyl-diphenyl ether were added to Fuel B. The lowest temperature at which the fuel passed the LTFT test was -13°C.

Comparative Example 9

In this test 0.06 weight percent ethylene vinyl acetate copolymer, 0.015 weight percent wax-naphthalene condensation product and 0.025 weight percent alkyl-diphenyl ether were added to Fuel B. The lowest temperature at which the fuel passed the LTFT test was -15°C.

Comparative Example 10

In this test 0.05 weight percent of dihydrogenated tallow amine salt of phthalic anhydride, and 0.025 weight percent of alkyl-diphenyl ether were added to Fuel B. The lowest temperature at which the fuel passed the LTFT test was -12°C.

Comparative Example 11

In this test 0.05 weight percent dihydrogenated tallow amine salt of phthalic anhydride, 0.05 weight percent wax napthalene condensation product, and 0.025 weight percent alkylated diphenyl ether were added to Fuel B. The lowest temperature at which the fuel passed the LTFT test was -14°C.

Example II

In this example about 0.038 weight percent of dihydrogenated tallow amine salt of phthalic anhydride, 0.012 weight percent ethylene vinyl acetate copolymer, 0.003 weight percent wax-naphthalene condensation product, and 0.015 weight percent alkyldiphenyl ether were added to Fuel B. This fuel passed the LTFT test at -20°C, thereby also demonstrating the utility of the present invention.

A summary of the LTFT test results for Comparative Examples 6-11 and Example II is presented in Table II. Here also it can be seen that the use of the four component system in Example II produced a fuel oil having a lower LTFT than any of Comparative Examples 6-11 even though the total weight percent of the additive used with the four component system of Example II was lower than the weight percent of additive used in Comparative Examples 6-11.

TABLE II

TEST DESC.	WEIGHT PERCENT ADDITIVE IN FUEL				TOTAL WT. % ADDITIVE IN FUEL	LOWEST TEMPERATURE FOR LTFT PASS, °C
	TAPA	EVA	WAX-NAPHTHALENE	ADPE		
Comp. E.G. 6	-	-	-	-	-	-9°C
Comp. E.G. 7	0.05	0.02	0.005	-	0.075	-13°C
Comp. E.G. 8	-	0.038	0.012	0.025	0.075	-13°C
Comp. E.G. 9	-	0.06	0.015	0.025	0.100	-15°C
Comp. E.G. 10	0.05	-	-	0.025	0.075	-12°C
Comp. E.G. 11	0.05		0.05	0.025	0.125	-14°C
Example 11	0.038	0.012	0.003	0.015	0.068	-20°C

Based on the results in Tables I and II, it can be seen that the addition to wax-containing distillate of all four components produced wax crystals which were sufficiently small to permit the fuel to pass through the filter pores at lower temperatures than would be possible using only two or three of the four components.

The individual components of the fuel additive of the present invention typically may be present in the following concentrations in the fuel:

ADDITIVE	WEIGHT PERCENT RANGE	PREFERRED WEIGHT PERCENT RANGE
Amide and/or Amine Salt of Carboxylic Acid/Anhydride	0.002-1.00	0.01-0.15
Ethylene-Containing Polymer/Copolymer	0.002-0.75	0.005-0.15
Wax-Naphthalene Condensate	0.001-0.50	0.002-0.10
Alkylated Diphenyl Ether	0.001-0.50	0.005-0.15

Fuel additives conventionally are sold as concentrates in solvent so that they can be easily added to the distillate fuel which is to be treated to improve its cold flow properties. Typically, a diluent is added so that the additive is a single phase liquid. A typical additive concentrate has the following composition:

ADDITIVE	WEIGHT PERCENT RANGE	PREFERRED WEIGHT PERCENT RANGE
Amide and/or Amine Salt of Carboxylic Acid/Anhydride	5-40	12-25
Ethylene-Containing Polymer/Copolymer	2-15	3-10
Wax-Naphthalene Condensate	1-10	1-3
Alkylated Diphenyl Ether	2-15	4-12
Diluent	20-95	35-75

A preferred diluent is a heavy aromatic naphtha. The additive preferably is added to the fuel at a temperature substantially above the wax appearance point, since the solubility of the additive in the fuel will be higher at elevated temperature.

CLAIMS:

1. An additive composition suitable for improving low temperature flow properties of a wax-containing petroleum distillate fuel, characterised by comprising:

A. an amide and/or amine salt of a carboxylic acid and/or anhydride;

B. an ethylene polymer and/or copolymer;

C. a condensation product of a halogenated paraffin or an olefin with an aromatic compound; and

D. an alkylated diphenyl ether.

2. An additive composition as claimed in claim 1, wherein component A comprises a C_{16}-C_{40} alkyl amine anhydride salt.

3. An additive composition as claimed in claim 2, wherein the C_{16}-C_{40} alkyl amine anhydride salt is selected from those of phthalic anhydride, maleic anhydride, succinic anhydride and mixtures thereof.

4. An additive composition as claimed in any preceding claim, wherein component B is a copolymer of ethylene and an unsaturated mono- or diester of the general formula:

$$\begin{array}{ccc} R & & H \\ | & & | \\ C & = & C \\ | & & | \\ R_2 & & R_3 \end{array}$$

wherein: (a) R_1 is hydrogen or methyl; (b) R_2 is a $-OOCR_4$ or $-COOR_4$ group; (c) R_3 is hydrogen or $-COOR_4$; and (d) wherein R_4 is hydrogen or a C_1 to C_{16} straight or branched chain alkyl group.

5. An additive composition as claimed in any preceding claim wherein component C comprises a wax-naphthalene condensation product.

6. An additive composition as claimed in any preceding claim, wherein component D comprises a diphenyl ether alkylated with an olefin having from about 16 to about 50 carbon atoms.

7. An additive composition as claimed in any preceding claim, comprising:

(a) about 5 to about 40 weight percent of component A;

(b) about 2 to about 15 weight percent of component B;

(c) about 1 to about 10 weight percent of component C;

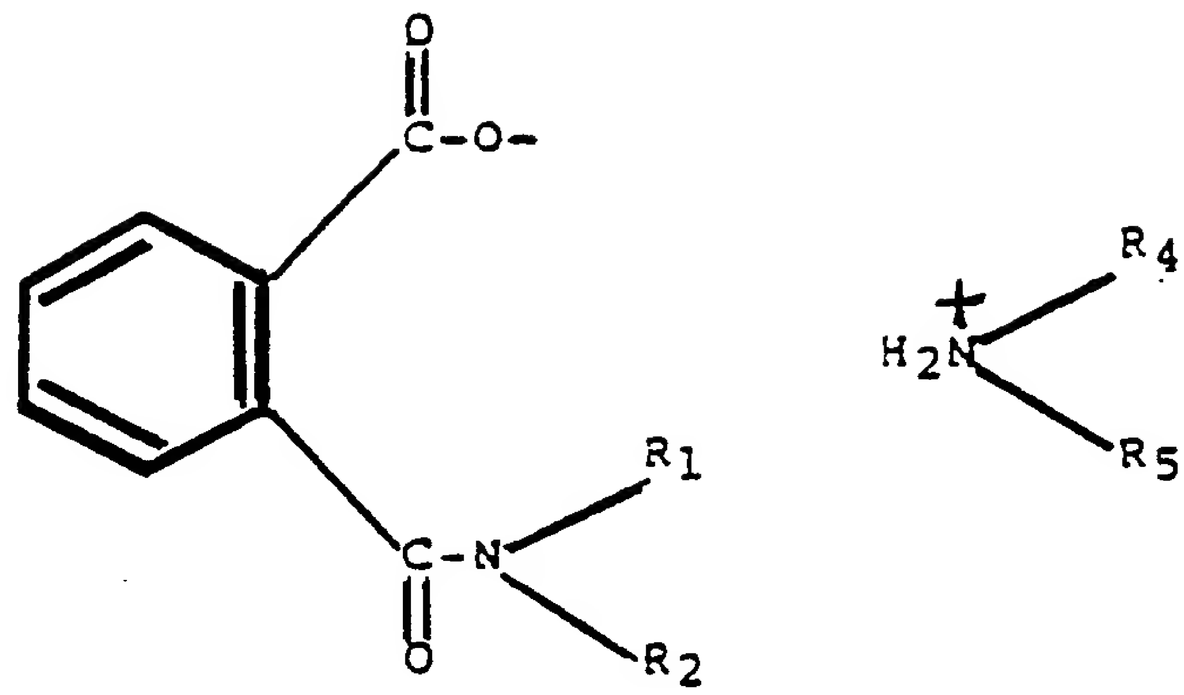
(d) about 2 to about 15 weight percent of component D; and

(e) about 20 to about 90 weight percent of diluent.

8. An additive composition as claimed in claim 8, wherein the diluent comprises a heavy aromatic naphtha.

9. A wax-containing petroleum distillate fuel, preferably having a boiling range within the limits 120°C and 450°C, containing the components A, B, C and D defined in any preceding claim.

10. A method for improving the low temperature flow properties of a middle distillate, preferably one boiling in the range of about 120°C to about 450°C, characterised by adding to the fuel an effective amount, preferably being at least about 0.005 weight percent of the fuel, of a composition claimed in any one of claims 1 to 8.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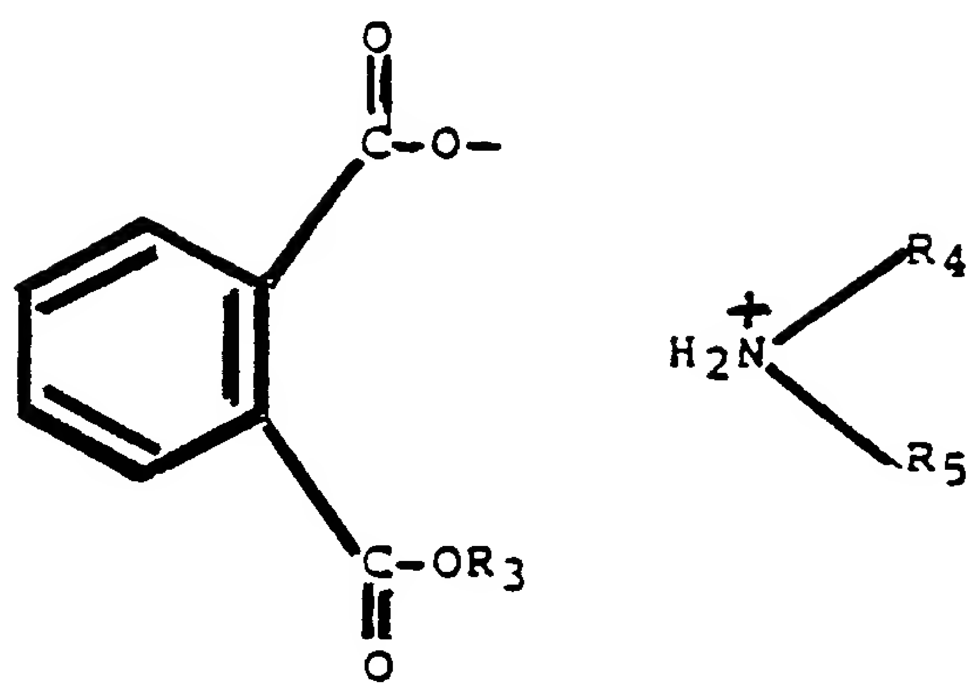
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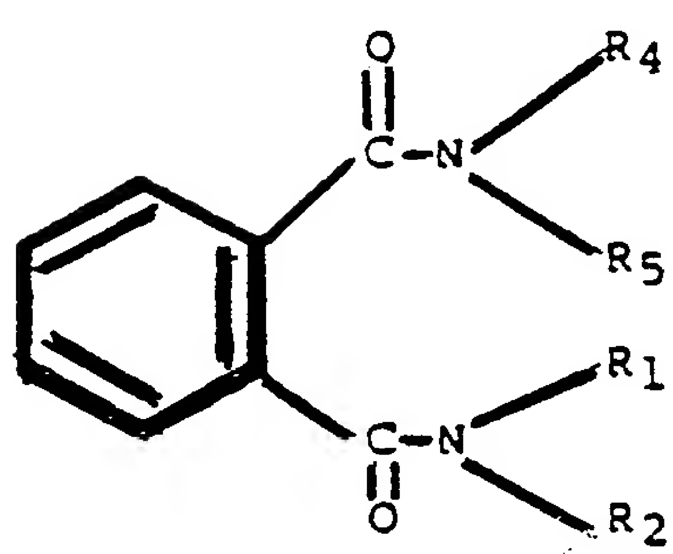
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EUROPEAN SEARCH REPORT

Application number

EP 86 30 4034

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
D,Y	FR-A-2 300 792 (EXXON) * Page 2, line 37 - page 3, line 31; claims 1-7 * ---	1-10	C 10 L 1/14
D,Y	US-A-4 014 663 (FELDMAN et al.) * Abstract; columns 2-4; columns 9-10; claims 1-14 * ---	1-10	
Y	US-A-4 210 424 (FELDMAN et al.) * Abstract; columns 2-6; claims 1-18 * ---	1-10	
A	EP-A-0 061 894 (EXXON) ---		
D,A	US-A-3 910 776 (FELDMAN) ---		TECHNICAL FIELDS SEARCHED (Int. Cl.4)
D,A	US-A-3 999 960 (LENGER et al.) ---		C 10 L
D,A	US-A-4 402 708 (OSWALD) -----		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	01-08-1986	LO CONTE C.

CATEGORY OF CITED DOCUMENTS

- X : particularly relevant if taken alone
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